

PULSED LASER DEPOSITION OF Ni-Zn FERRITE THIN FILMS

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Thin $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite films were grown on different condition on different substrates using pulsed laser deposition technique. Studying the influence of the energy of the laser beam, of the O_2 pressure, of the substrate temperature, and of the distance between the target and the substrate on the microstructure and on the magnetic properties were established optimal conditions for PLD of ferrite thin film on silicon. The microstructure of the thin films was characterized by SEM, EDS, AFM and XRD analysis. The magnetic properties were inferred from vibrating sample measurements. The magnetic behavior of the samples was interpreted in terms of the role played by post annealing condition on the microstructure.

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1. Introduction

Ni-Zn bulk ferrites are widely used in electronics because of high resistivity and high permeability at high frequency. Soft magnetic thin films with high electric resistivity are needed for developing microinductors and microtransformers [1]. The Ni-Zn ferrite is also used in discrete microwave devices. For integrated planar circuits operating at high frequencies however, designs based on thin ferrite films are expected to have important application. An important step in realization of planar ferrite devices is the study of the influence of the microstructure on the magnetic properties.

Attempts have been made by researchers to deposit NiZn ferrite thin films by different techniques such as rf sputtering, pulsed laser deposition, and facing target sputtering [2,3,4]. There are also reports on an alternative method of preparation of NiZn ferrite thin films by spin-spray ferrite plating [5,6,7]. The innermost processes in deposition of the magnetic thin films are not well understood. An attempt to understand the anomalous variation of coercivity with annealing in nanocrystalline NiZn ferrite films was made in [8]. The NiZn ferrite thin film in this case was prepared by rf sputtering and the evolution of magnetic properties as a function of annealing temperature was studied.

High quality single-crystal ferrite films are useful for many magnetic devices that require low magnetic losses and/or tailored magnetic properties. Currently, ferrite thick films can be grown using pulsed laser deposition (PLD) [9]. The XRD results indicate in this case a significant amount of compressive stress in the as - deposited PLD Ni-Zn ferrite films. The stress manifests itself as a stress induced planar magnetic anisotropy field due to the distortion of the cubic unit cell of Ni-Zn ferrite. There are several possible sources contributing to the large amount of stress that is present in the PLD Ni-Zn ferrite films. The most significant factor is the oxygen pressure during growth, which affects the unit cell volume and stress of the film. At low pressure oxygen diffuses out of the newly deposited

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layer producing an oxygen deficiency in the film, which causes an expansion of the unit cell. A large stress results because the film has been already bonded to the substrate or underlying film layer, and this constraints the expansion of the unit cell in the film plane. At high oxygen pressure, there is considerably less diffusion of the oxygen out of the film so the dimensions of the unit cell do not change significantly during deposition and, consequently, there is less film stress.

Other factors that could contribute to the stress include differences in the coefficient of thermal expansion and lattice mismatch between film and substrate. During PLD deposition at high temperature, delamination processes were observed. The lattice mismatch, which is 0.7% between the MgO and Ni-Zn ferrite, should not be significant in the thicker ferrite films (10 – 15 μm).

A relatively high substrate temperature of 700 °C is necessary for increased mobility in order to achieve high quality crystalline film on (100) MgO substrate with nearly bulk saturation magnetization values. Lower temperature would be more desirable in order to make the process compatible with semiconductor substrate such as GaAs. The largely smooth surface morphology at low pressure is necessary for device patterning but the delaminated regions due to the increased film stress are limiting factors for practical applications. The very rough surface morphology, due to the polycrystalline grains, are not acceptable for practical microwave devices. The microstructure of the thin films growth at low oxygen pressure are highly stressed because of the lack of the oxygen atoms in the lattice [10]. At high pressure all the preferential sites are occupied by oxygen atoms and the thin film has low anisotropy induced by internal stresses. The stress induced planar anisotropy field is not desirable because the magnetization of the film normal to the plane, which is the configuration used in the most microwave ferrite film devices, requires applied magnetic field several thousands Oe larger than the expected $4\pi M_s$ value. Larger applied magnetic fields are necessary in order to overcome the stress induced planar anisotropy field.

The nature of the targets plays an important role in the PLD process. The temperature of the sintering process influences the microstructure and magnetic properties of the targets. The microstructure of the targets sintered at low temperature is homogenous and the average grain size is in the nanometer range. Therefore the surface of the PLD ferrite films is smooth [11]. The saturation magnetization of the targets is lower due to the soft sintering process and consequently the saturation magnetization of the PLD ferrite films is low. The Ni-Zn ferrite films grown by PLD from targets sintered at high temperature are characterized by average grain size in the micrometer range [12]. The laser pulse energy density is low in the case of droplet formation. The coercive field is larger than that found for bulk material, as a direct results of the anisotropy originating in the film microstructure of the film grown on quartz substrate.

This paper is focused on the PLD of Ni-Zn ferrite films on different substrates (silicon, glasses or quartz). The temperature of the substrates and the post deposition thermal treatment temperature is limited by experimental conditions or technological requirements. The temperature of the substrates is a very important factor for the microstructure of the films. The main purpose of this work is to clarify the influence of the substrate and of the temperature of the substrate on the microstructure of the Ni-Zn ferrite films. Scanning electron microscopy (SEM), energy dispersive X ray analysis (EDS) and atomic force microscopy (AFM) have been used to observe the microstructural and morphological characteristics, to which the quality of the film is highly sensitive. The film structure was determined by X-rays diffraction analysis (XRD) and compared with that of the bulk material. The magnetic properties were studied by vibrating sample magnetometer (VSM) measurement. The results are interpreted in terms of the role played by the PLD parameters and of the post annealing process on the microstructure and magnetic properties of the thin ferrite films.

2. Experimental results

The Ni-Zn ferrite with nominal composition $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ used as target for PLD was prepared by the usual soft ceramic technique [11]. The appropriate mixture of $\alpha\text{-Fe}_2\text{O}_3$, NiCO_3 , Ni(OH)_2 , H_2O and ZnO was milled in a steel ball-mill for 3 hours using demineralized water. The drying mixtures were presintered at 850 °C for 3 hours, in air. The X ray pattern of the presintered

powder contains diffraction peaks specific to the spinel phase as well as lines ascribed to precursors like α -Fe₂O₃ and ZnO. The presintered powder was milled in a steel ball-mill for 2 hours in demineralized water. The milled and presintered powders porosity was measured using BET surface area analyzer. In this methods is determined the quantity of water or gas absorbed by powders in specific condition (isothermal methods). The measured value was $4.3 \pm 0.3 \text{ m}^2\text{g}^{-1}$. Using polyvinyl alcohol (PVA) as a binder the powders were dry pressed into pellet shape having diameter and thickness of 28 mm and 6 mm, respectively. The green density of all specimens was $3.1 \pm 0.2 \text{ gcm}^{-3}$. After pressing, the pellets were sintered at 1100 °C for two hours in air and cooled in nitrogen atmosphere with less, than 0.1%O₂. The sample densities were measured using Archimedes method.

The structure of the targets was determined by X-ray diffraction using the SCINTAG DMS 2000 XRD machine provided with Fe target ($\lambda\text{FeK}_{\alpha}=1.93604 \text{ \AA}$) in the angular range 2θ of $10^\circ - 90^\circ$. 2θ for Fe K_α radiation were transformed to the 2θ CuK_α radiation and the data were plotted in the angular range of $20^\circ - 80^\circ$. The XRD pattern taken in the conventional $\theta - 2\theta$ method mode, shows that the target is single phase.

An excimer laser, Lambda Physik model COMPex 102 operated with KrF active mixture ($\lambda = 248 \text{ nm}$) giving 20 ns pulses was used for PLD. The films were grown with a pulse energy in the range of 65 –75 mJ, at a repetition rate of 10 Hz. The laser beam was directed at 45° from the target normal and focused on a $3.5 \times 0.5 \text{ mm}^2$ area of the ablated target. A simple mechanical system was used to raster over the target surface the laser beam. Different substrates as (100) silicon, (100) Al₂O₃, (100) MgO, (100) SrTiO₃ and glass (microscope slide, corning glass) were used. The substrate size was 10 mm $\times$ 20 mm for silicon and glass and 10 mm $\times$ 10 mm for Al₂O₃, MgO and SrTiO₃ substrate.

The deposition of the NiZn ferrite thin films was done in a stainless-steel high-vacuum chamber, as described elsewhere [13], where a base pressure lower than 0.13 mPa (1×10^{-6} Torr) was achieved with a turbomolecular pump. The substrate was mechanically attached to the substrate holder mounted at 4 cm from the target and placed parallel to it inside IR heater assembly, which was capable of raising the temperature of the substrate to over 700 °C. The substrate temperature was monitored and controlled with a thermocouple in contact with the surface of the substrate holder. The gas pressure inside the PLD chamber was measured using a cold cathode gauge and adjusted via an electronic mass flow controller. Flowing O₂ gas pressure ranging between 0.13 and 30 Pa (1 and 200 mTorr) was used. The substrate temperature during deposition was between 400 – 600 °C. Before deposition, the substrates were cleaned for 15 min in acetone in an ultrasound bath, then rinsed and soaked. To diminish the occurrence of ferrite drops, which might be splashed out from the target during laser ablation, the process was done under constant energy of the laser beam. The ablation spot was permanently rastered on the target surface to ablate fresh material and avoid the effects of target cratering. The deposition time was varied from 30 min to 2 hours. The thickness of the films was determined with a profilometer with 5 Å resolutions. *Ex situ* post deposition thermal oxidation was performed at 1100 °C, for 2 h, under the conditions of rapid heating up and cooling down rates (15 °C/min).

The film structure before and after annealing process was characterized using XRD, SEM on a Hitachi S3000N microscope equipped with a Horiba EDX microprobe and AFM on a Quesant Q-Scope 350 microscope for surface texture and grain size. The room temperature magnetization M_s and the coercive field were measured by vector VSM Lakeshore 7307, located at University of New Orleans, with dc magnetic field applied parallel and perpendicular to the film plane, and then compared with those of the targets.

3. Results and discussion

The morphology of a typical film, which visibly shows a smooth surface of good definition and optical quality, is presented in the SEM picture of Fig. 1, and in the AFM image of Fig. 2. The droplet contamination, usually associated with the PLD process [14, 15], is rare. The occurrence of

these few ferrite droplets is the result of incomplete elimination of target splashing during laser ablation, in spite of lower energies of laser beam. High repetition rate of the laser pulses, which is required to assure high deposition rate, may cause droplets and cluster aggregates occur during ablation [16]. We found that 5 Hz is an optimum repetition rate for growing good quality Ni-Zn ferrite thin films. The deposition rate was about 3 nm/min. An increase in grain size was observed as a result of increasing the substrate temperature. This feature can be attributed to an increase in atomic mobility in as deposited films. The post annealing process determine a nucleation process and polycrystalline structure films can be observed in all the cases. Different average grain size, near the submicrometer range, is the result of different PLD process parameters and various annealing temperatures.

The average composition of the film was determined by EDX studies using systematic data collected from the centre, middle and edges of the films. The relative elemental concentration were used to estimate the atomic composition of the as deposited and annealed film, by considering their values normalized to the nominal composition of the target. The composition of the films was found to be close to the composition of the target. Fig. 3 presents the EDX analysis for Ni-Zn thin film deposited on a Si substrate. The Ni, Zn, Fe and O peaks appear along with a large Si substrate peak. The evolution of the oxygen peak in the EDX spectra showed increasing values for the oxygen signal after thermal oxidation at 1100 °C. The SEM micrographs stand for increasing the grain size by nucleation.

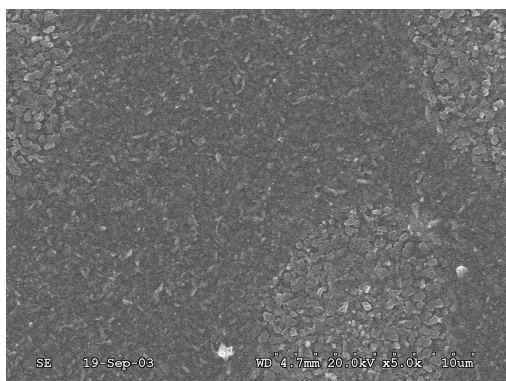


Fig. 1. SEM micrograph of the Ni-Zn ferrite film deposited at 600 °C and annealed at 1000 °C.

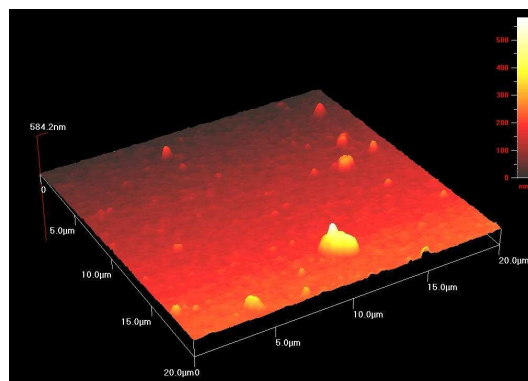


Fig. 2. AFM image of the Ni-Zn ferrite film as deposited at 600 °C.

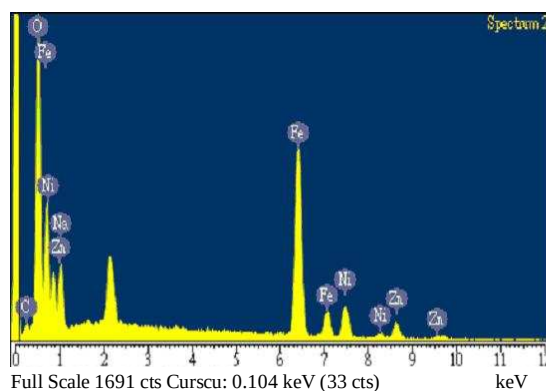


Fig. 3. EDX spectrum of the Ni-Zn ferrite film grown on Si, and annealed in oxygen for 2 hours at 1100 °C.

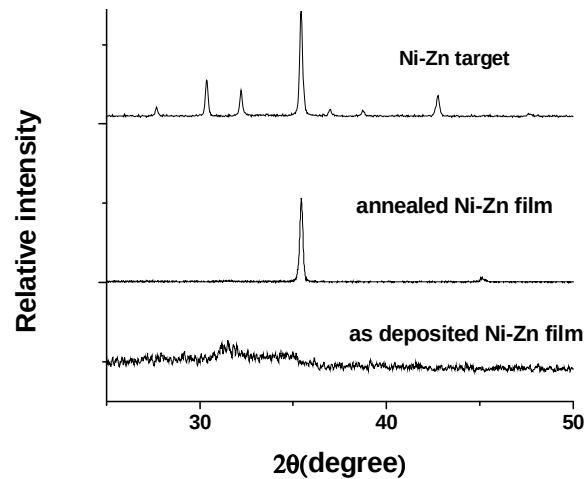


Fig. 4. XRD pattern for the Ni-Zn ferrite target and film grown on silicon (as deposited) and annealed in oxygen for 2 hours at 1100 °C.

The film structure for films grown at low temperature, as determined by XRD and SEM, shows small crystalline island insulated by large amorphous regions. Post annealing XRD patterns points out for phase transformation and predominantly (311) textured structure for the films grown onto silicon substrate (Fig. 4). In the case of Ni-Zn ferrite grown onto glass substrate an amorphous hump near 22° was observed. Similarly synthesized NiZn ferrite films made onto Al_2O_3 substrates exhibited small and broadened diffraction lines, which could be sharpened only by subsequent heat treatments.

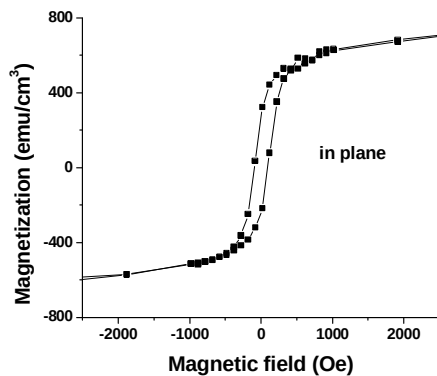


Fig. 5. VSM magnetization loops of Ni-Zn ferrite film measured in plane.

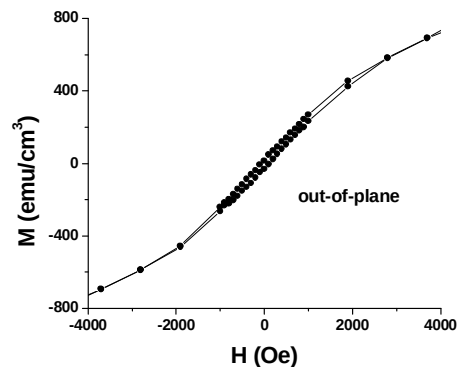


Fig. 6. VSM magnetization loops of Ni-Zn ferrite film measured out-of-plane (perpendicular to the film plane).

Room-temperature magnetic hysteresis loops were measured for the bulk ferrite, as deposited and annealed films. Typically in plane and out-of-plane magnetization curves are shown in Fig. 5 and 6 for the film post annealed at 1100 °C in oxygen for 2 hours. The saturation magnetization was found to be 620 emu/cm³ which is close to the value for the bulk material suggesting stoichiometric Ni-Zn ferrite. The (311) Ni-Zn ferrite textured film grown on oriented silicon substrate indicates a coercive field of 98 Oe larger than the value found for the target, and this can be attributed to crystallite shape anisotropy, which includes extrinsic properties such as the grain size. The SEM and AFM micrographs indicate a smaller grain size in the film, as compared with the target. The magnetic behavior of the Ni-Zn ferrite films is in accordance with the microstructural data.

It is important to point out that in a recent paper [17] we have studied the morphological, structural and magnetic properties of Ni ferrite deposited by PLD. The results are very similar to those obtained on the Ni-Zn ferrite, and reported in this paper.

4. Conclusions

There were investigated the morphological, structural, and magnetically properties of Ni-Zn ferrite thin films grown by PLD on various crystalline and amorphous substrates at different substrate temperature and different gas pressure in order to establish the optimal condition for smooth thin film. As deposited the thin films are often composite: crystalline island lapped by the amorphous phase. After annealing the amorphous Ni-Zn ferrite thin films become textured. The texture is influenced by the conditions of the deposition process, by the nature of the substrate and by the thermal treatment. The film composition is found to be that of the target. The XRD patterns of the films grown on silicon after annealing process evidence a (311) textured structure. This structure exhibits magnetic properties. The coercive magnetic field is larger than that found for the bulk material, and this feature is due to the crystallite shape anisotropy originating in the film microstructure, while magnetization value are close to the bulk magnetization.

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